

# SIRMS Studies on the Repassivation of Aluminum Exposed to Dichromate Solution

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Beamline(s): U10B

**Introduction:** Chromates, even in very low concentrations have been shown to increase the polarization resistance of AA2024-T3 by a few orders of magnitude<sup>1</sup> and hence are considered to be efficient inhibitors. Chromate conversion coatings (CCC) or paints containing chromates have self-healing properties, which have been associated with migration of these chromates to actively corroding sites<sup>2-3</sup>. Scratch and chromate migration studies on aluminum have been performed using AFM<sup>4</sup>, Raman spectroscopy<sup>2</sup>. In this work we explore the repassivation of a scratch on pure aluminum using Open Circuit Potential (OCP) measurements, Synchrotron InfraRed MicroSpectroscopy (SIRMS).

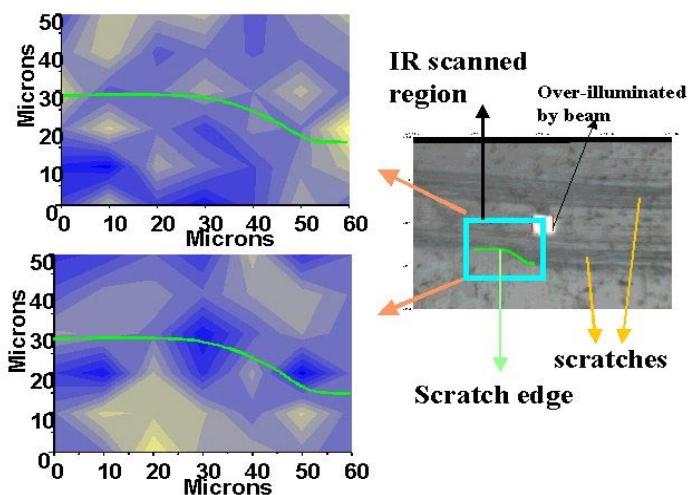
**Methods and Materials:** Al (99.999%) was exposed to a 0.025 M solution of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) for a period of 300 s. This is approximately the same individual concentration of dichromate and time of treatment for a commercial conversion coating. This was then rinsed well in de-ionized water followed by drying with nitrogen. The sample (1  $\text{cm}^2$ ) was immediately exposed to a 0.05 M NaCl and the OCP was monitored. During this time the sample was scratched and allowed to repassivate several times. A SIRMS mapping was performed on the scratch using the U10B UV beamline at Brookhaven National Laboratory.

**Results:** The chemical mapping performed using SIRMS shows the qualitative presence of chromate and aluminum oxide. Initial results obtained from the analysis are shown for dichromate and aluminum oxide. **Figure 1** shows the mapping of dichromate ions ( $934\text{ cm}^{-1}$ , corresponding to point group of  $\text{C}_{2v}$ , Handbook of Infrared and Raman spectra, Vol. 3, p 139, ID 233) and for aluminum oxide ( $724\text{ cm}^{-1}$ , Handbook of Infrared and Raman spectra, Vol. 4, p 208, ID 319). These form the most intense absorption frequencies for these two species. It can be seen that migration of chromium occurs to the edge of the scratch. The aluminum oxide map shows very low concentrations of aluminum oxide, if any, on the edge of the scratch. This can be explained due to the fact that

edge of the scratch forms a highly active region due the intense plastic deformation that would have occurred during the scratching. This might also confirm the theory that fluoride ions accelerate the formation of a chromate coating by active destabilization of the highly passive oxide film. Hence the absence of a high concentration of aluminum oxide is understood. However, it should be realized that these are qualitative mapping indicating the relative distribution of the

$\text{Cr}_2\text{O}_7^{2-}$   
distribution on the  
region shown in  
the scratch.

$\text{Al}_2\text{O}_3$   
distribution on  
the region  
shown in the  
scratch.



**Figure 1.** The chemical mapping shows the qualitative presence of chromate and aluminum oxide.

species in the mapped area. Analysis for the relative distributions of aluminum hydroxides and other chromium species are under progress and will be included in the next report. The duplex model put forward last year<sup>5</sup> predicts the formation of a Al (III)-Cr(VI) complex in the pits and this shall be verified following the completion of the analysis of data obtained from NSLS.

**Conclusions:** These studies indicate the migration of hexavalent chromium from coatings to actively corroding sites. These results also confirm the self-healing properties of chromate conversion coatings.

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**References:** <sup>1</sup>D. Chidambaram, M. J. Vasquez, C. R. Clayton and G. P. Halada, "Study of the Electrochemical Behavior of Intermetallic Particles in AA2024-T3", 197<sup>th</sup> Meeting of the ECS, abstract 212, May 16 (2000); <sup>2</sup>J. Zhao, G. Frankel and R. L. McCreery, J Electrochem. Soc. **145**, 2258 (1998); <sup>3</sup>J. D. Ramsey, R. L. McCreery, J Electrochem. Soc. **146**, 4076 (1999); <sup>4</sup>P. Schmutz and G. S. Frankel, J Electrochem. Soc. **146**, 4461 (1999); <sup>5</sup>C. R. Clayton, G. P. Halada, D. Chidambaram and M. J. Vasquez, in *Passivity and Localized Corrosion*, M. Seo, B. MacDougall, H. Takahashi and R. G. Kelly, editors, PV 99-27, p. 249, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).